

Development of robust mixed-conducting membranes with high permeability and stability

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Abstract

This chapter presents an illustration of the current state of the art in the development of mechanically and chemically robust perovskite-based membranes featuring industrial application. Without pretending to give an exhaustive picture of all developments in the field the principal points of interest are discussed and the most recent concept summarized. Finally, brief guidelines for possible future studies are proposed.

Keywords: perovskites, mixed -conducting membranes, robustness, chemical stability, mechanical properties

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1. Overview

Literally almost 90 % of the periodic table can form perovskite compounds with ideal compositional formula of $A^{2+}B^{4+}O_3$ being the compositions $A^{1+}B^{5+}O_3$ and $A^{3+}B^{3+}O_3$ also possible if the total charge of the A and B cations equals that of oxygen [1,2]. The A-site cation can be a rare earth, alkali or alkaline earth ion, such as La, Na, Ca, Sr or Ba, while the B-site is a transition metal, such as Ti, Zr, Fe, Co, Ni or Cu [3,4].

The perovskites cubic structure allows partial substitution of A and B cations by other cations with different ionic radius size and valence [4]. This substitution, however, could result in other structures formation, such as orthorhombic or rhombohedral. Other effect of the substitution is the perovskites nonstoichiometry, resulting from A, B or O site deficiency or excess. The A and O sites could be partially empty with preserving the perovskite structure, on the contrary to the smaller energetically unfavorable B sites. Thus compounds of interest are principally of $ABO_{3-\delta}$ type where the δ parameter is envisaged as the number of vacancies or defects and it is directly associated to the oxygen permeation capacity of the perovskite [5]. Adequate metal substitutions at the A and B sites could carefully tailor the conduction properties. Substitution at the A sites are related to the oxygen vacancies concentration, while substitutions at the B sites are responsible for the electron conductivity. In these mixed conductors, the ionic conductivity takes place in these materials by the so-called hopping mechanism in which oxide ions move from oxygen vacancy to oxygen vacancy, besides this, electronic conduction occurs through $B^{n+}-O-B^{(n+1)+}$ pairs formed to assure the overall electroneutrality of the material. Therefore, materials of $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$ composition results in mixed conductors whose conductivity depends on the nature of the doping cations [1,2]. The defect chemistry of perovskites marks their application. Its capacity to

keep the structure although slightly deformed to accommodate different charges, allows continuous properties adjustment, e.g. high degree of oxygen non-stoichiometry and high ionic, electronic and even protonic conductivity [6-12]. All those features convert perovskites and perovskite-like materials in useful ceramic membranes for oxygen transport processes with potential applications in chemical reactions with academic and/or industrial interest.

Nowadays mixed ionic-electronic conducting membranes (MIEC membranes) based on perovskites awakens the industrial interest as inexpensive large-scale oxygen production alternative of the currently available cryogenic distillation. The application of MIEC membranes based technologies are judged crucial for the development of the next generation of integrated carbon capture and sequestration power plants based on coal gasification or oxy-fuel coal combustion technologies [13-15]. To these two future application the most noteworthy industrial applications of MIEC systems nowadays have to be underlined, the oxygen production for power from fossil fuels in oxy-fuel power plants [13,16] and the integration in a high temperature catalytic membrane reactors for methane or alkenes upgrading by selective oxidation, as for example partial oxidation of methane (POM) to produce syngas [14,17-20].

Facing future industrial applications the perovskite-based membranes should fulfill the following requisites:

- i) high oxygen flux, usually controlled by the composition, the defect chemistry of the perovskite and the membrane thickness, the thinner the membrane the higher the flux.
- ii) high thermal stability, the phase transition from cubic to other crystal structure have to be avoided in order to maintain high oxygen flux

iii) the membranes should be dense (absence of porosity), so the oxygen diffusion could occur only if the driving force (oxygen partial pressure gradient) is present

iv) the membranes should be mechanically and chemically robust

v) all engineering aspects, such as reliable design for plant scale application including geometries, sealing and cost have to be subaltern to every independent process.

Some of these requisites are still considered challenges. There is, without any doubt, urgent necessity for the development of mechanically and, especially, chemically robust finely designed highly performant membranes for industrial application. This chapter will be devoted to the summary of the very recent improvements proposed and reported in the literature dealing with the development of chemically and mechanically robust membranes. Due to the large variety of available perovskite-based membranes, only the ones most frequently cited in the literature will be considered, the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) and $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (BSCF). In particular, the highest known oxygen permeation rate of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) makes it one of the most preferred materials for oxygen permeation flux studies. In this material, the half of Ba^{2+} ions are replaced by Sr^{2+} ions both are in the A sites of the structure, while the B sites are occupied by cobalt and iron cations [5,21]. However the BSCF membranes, at temperatures below 900°C , suffers oxygen flux diminution caused by a gradual transformation of the cubic crystal phase to hexagonal which limits the membrane integration in this temperature range [22, 23]. In spite of this instability the oxygen flux can be recovered by treatment at higher temperature in inert sweep gas to induce the cubic structure recovery [24, 25]. This inconvenient could be easily solved by the use of LSCF family characterized by its good phase stability and mechanical strength. This family is derived by the pioneer Teraoka's $\text{SrCo}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ oxygen permeable perovskite,

where the La^{3+} ions partially substitute the Sr^{2+} ions in the A sites [26-28]. Nowadays the LSCF normally refers to the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ composition.

2. Mechanical robustness

A future application of the membranes with optimized oxygen flux will demand on first place a good mechanical stability. In general manner, the mechanical properties will impose restrictions on membrane design and operating temperatures. Despite of the extensive amount of scientific information available in the literature concerning the perovskite membranes design just a small part of it is related to the mechanical properties of the membranes. Nevertheless the fracture mechanics gains importance as the scaling-up of the membranes becomes to the focus, the mechanically robust materials and designs are needed.

The mechanical properties could not be improved without knowing the particularities of the system. The perovskite structure expands as a result of oxygen vacancies creation, establishing a chemical internal strain during this process, which might cause failure of the membrane [29]. On the other hand the mechanical behavior is strongly related to the occurrence of phase changes. For example, the presence of redox active cobalt in both families, potentially unstable in reductive atmospheres, could cause cubic to non-cubic transition according to its reduction rate. The oxygen permeability appears then deteriorated and its thermal expansion coefficient is also influenced (increases in comparison to that of the perovskite) which introduces stress across the membrane and produces mechanical failure. The mechanical properties of BSCF and LSCF have been studied systematically at elevated temperatures. Defects in the elastic behavior were observed for both families and the elastic anomalies were attributed to a Co^{3+} spin transition [30, 31]. The Fe ions also were reported to present an antiferromagnetic to

paramagnetic transition in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ [32]. In both cases, the spin transition causes an electron reorientation resulting in an internal lattice stress.

Recently, Huang *et al.* [30, 33-35] reported various studies of the most important mechanical properties of BSCF and LSCF membranes, summarized in **Figure 1**. They analyzed the apparent fracture toughness of a polished membrane cross-section by indentation tests at room temperature after an annealed treatment. One side of the membrane was exposed to vacuum ($P_{\text{O}_2} = 2\text{mbar}$) and the other side to ambient air.

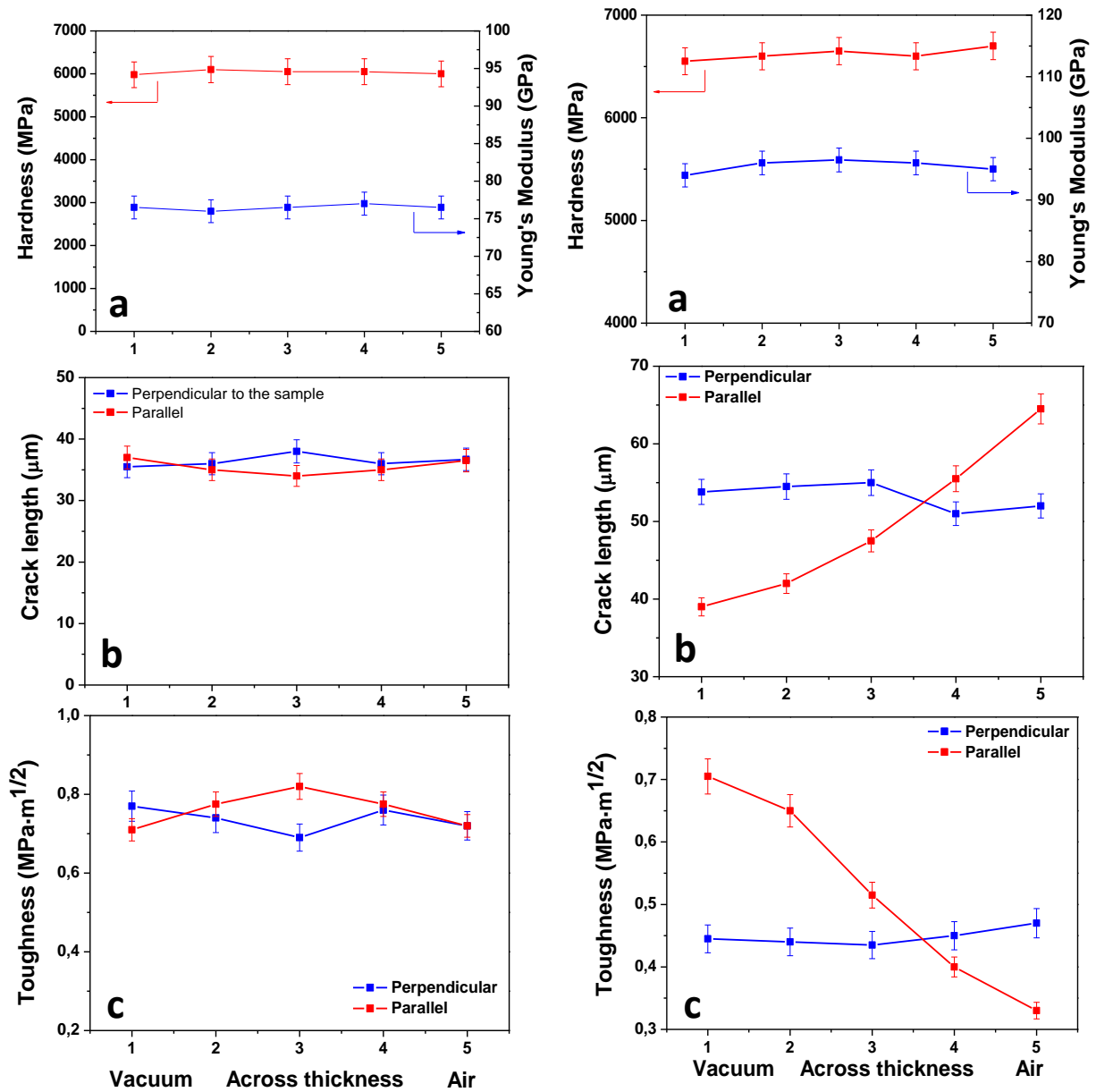


Figure 1. Properties of BSCF (left) and LSCF (right) across the thickness: (a) elastic modulus and hardness, (b) crack length, (c) fracture toughness, adapted from [33]

The elastic modulus and the hardness remain constant across the membrane thickness for both groups of perovskites. However, for LSCF, a chemical strain causing toughness and crack length variation through the membrane thickness was observed and related to the LSCF structure transition of from rhombohedral to cubic symmetry at 700 °C during the heating process and its difficulty to relax the stress when the cooling down process occur, thereby creating internal stresses. The annealing process also influences the fracture toughness for both membranes [34]. Three different methods for evaluation of the fracture toughness were applied and showed constant value for BSCF perovskite but variable for LSCF materials.

As the oxygen flux is a specific parameter that depends on the membrane thickness and surface activity, the mechanical robustness is strictly connected with the thickness and geometry of the membrane. An increase of the flux can be achieved either by reducing the membrane thickness or by increasing the surface area [2]. The mechanical robustness depends then on the maximum thickness reduction, which is related to the critical fracture stress of the material. In order to obtain more robust material, a thin membrane layer is often deposited on robust porous substrates of diverse geometries. These composites, also called asymmetric membranes, allow the physical diffusion of the oxygen through the porous support and its electrochemical permeation through the membrane dense layer (Figure 2). The mechanical reliability of such bi-layered composite will depend on the mechanical stability of the substrate and on the structural integrity of the membrane/substrate interface. Often a combination of the two LSCF and BSCF family perovskites are proposed as bi-layered composite [36-38] and

interestingly, composites of the same composition bilayers have received low attention up to date.

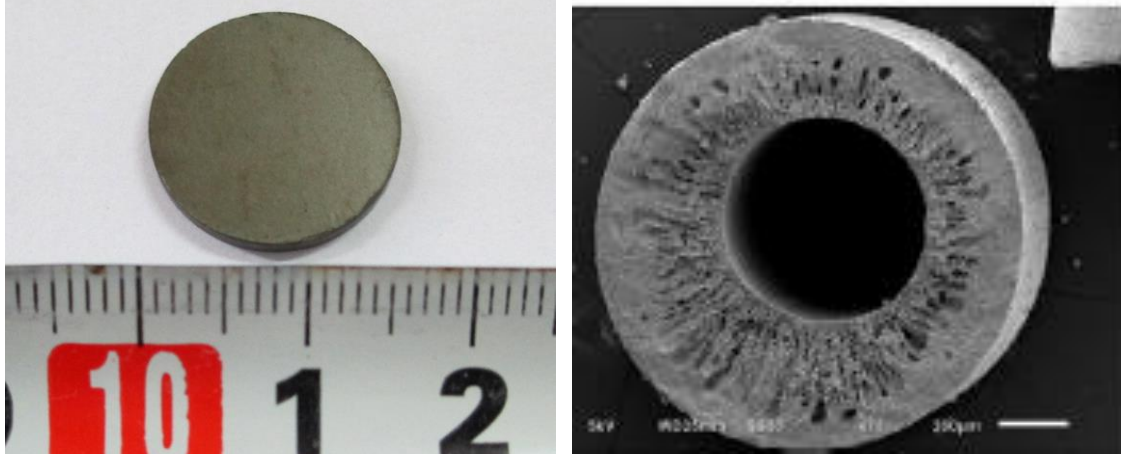


Figure 2. Planar and hollow fiber robust porous substrate, reprinted from ref. 39 and 40.

Meng et al. [39] recently proposed the two step fabrication of $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ asymmetric membrane in which the later presents a sufficient mechanical strength as a substrate (43.84 MPa) and a stable $4.51 \text{ ml (STP) cm}^{-2} \text{ min}^{-1}$ oxygen flux through the $20 \mu\text{m}$ thick $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ dense layer. Logically when the nature of the porous substrate and that of the membrane is the same the final material should present an important advantage. Nevertheless the thermal expansion coefficient of the perovskite materials is often not linear with the temperature and strictly materials specific [30, 41].

In the last decade variety of porous substrates are proposed for supporting the dense membranes, such as ceramics or metals and alloys [42-44]. Special interest in these studies is paid to the LSCF coating on metallic substrates achieved by physical methods such as plasma spray physical vapor deposition and magnetron sputtering as an alternative to the wet chemical methods of deposition [43, 44]. When considering

ceramic substrates besides the elastic behavior and the thermal expansion of the perovskites, other properties as toughness and fracture need to be identified as a function of temperature. It is important to underline that the fracture stress has to be assessed statistically in the case of ceramic materials, e.g. using characteristic strength and Weibull modulus. These two parameters together with the size of the component allow the determination of the failure probability for any applied intrinsic or extrinsic stress level [45].

The phase stability also could influence the mechanical robustness. A way to prevent the phase transformation and subsequent mechanical failure is the addition of protective coatings [38, 46, 47]. Vivet et al. [47] reported the change of the rate limiting step of permeation from surface exchange for the unmodified membrane to a balance between surface exchange and bulk diffusion which leads to increase of the oxygen flux with almost one order of magnitude.

Membrane geometry is other factor that influences their mechanical properties. Membrane geometries could be classified in four main groups, tubular, hollow fiber and capillaries, flat membranes, and multi-channel monoliths [48]. Initially, the flat membrane geometry presents the lowermost generated chemical stress due to its bending capacity and possible deformation to spherical cap. However, supporting of the thin flat membrane on porous substrate is totally constrained and does not allow the relaxation upon chemical stress by bending or extension [49]. So, despite the fact that flat membranes can bend to relax the internal stresses, there is no particular advantage of this conformation over the tubular geometry. Vente *et al.* [50], in a recent study, discuss the main advantages and disadvantages of both geometries assessing their specific surfaces and concluding that tubular membrane structure presents the most promising behavior. The tubular geometry presents higher specific surface and it is

more resistant to externally applied stress or temperature gradients [51]. Blond and Richet [52] determined the stresses in tubular membranes using finite element analyses paying attention to the heat transfer and bulk diffusion. Kwok et al. [53] studied the membrane fracture under compressive stress and its corresponding failure and the stress due to thermal distortion, external pressure and stoichiometric expansion gradients. Nevertheless, the superior surface to volume ratio in comparison to the flat membranes this geometry cannot bend to reduce the generated chemical strain and suffers three predominant stresses in the axial, radial and tangential directions. The hollow fiber geometry then takes the advantage on the tube geometry due to its ability to be produced with thinner membrane walls, retaining a good mechanical strength and providing higher surface to volume ratio and as a consequence increased oxygen flux. Zolochovsky et al. [54,55] investigated the influence of the membrane thickness and kinetic phenomena on the generated chemical stresses in hollow fiber membranes concluding that, in general, stresses in a membrane depends strongly on the oxygen surface exchange kinetics on the permeate side, which increases with the decrease of the membrane thickness.

Although the important volume of efforts dedicated to the mechanical properties improvements, nowadays on the threshold of massive industrial application of the perovskite membranes, the increase of the chemical stability is the most important aspect, as the supporting of the membranes appears to provide an acceptable solution of the mechanical problems. In the next part the principal developments to palliate this problem are described.

3. Chemical robustness

MIEC membranes can be applied in a broad variety of chemical processes [56]. In particular, the most noteworthy industrial applications of MIEC systems nowadays are the oxygen production for power from fossil fuels in oxyfuel power plants [13,16] and the integration in a high temperature catalytic membrane reactors for methane or alkenes upgrading by selective oxidation, as for example partial oxidation of methane (POM) to produce syngas [14, 17-20]. However working under real conditions involves the presence of CO_2 , SO_2 , H_2O , CH_4 and possibly other reductive compounds. All those compound challenge the chemical stability of the membranes. Perovskites are chemically unstable under large chemical potential gradients (for instance air/methane) and in the presence of the above-mentioned molecules the oxygen flux and the mechanical integrity of the membrane tend to decrease [2]. The vulnerability of the BSCF and LSFC type membranes under CO_2 , SO_2 and reductive atmosphere will be discussed and the most recent approaches to overcome the chemical stability limitations described.

3.1 Tolerance towards CO_2

The effect of CO_2 on the membranes performance must be necessarily examined for any practical application since CO_2 is contained in natural gas as well as a product in the oxyfuel and gasification reactions. Particularly, the demand of robust membranes against CO_2 is becoming significant in the so-called zero emission plants in which oxygen-permeating membranes are flushed with CO_2 as sweeping gas. Following the discussion of this chapter, the attention will be, in particular, focused on the BSFC and LSCF perovskites, although some comments on different types of ceramic membranes are included.

For BSCF, the state-of-art material with the greatest permeation flux, the poisoning effect of CO₂ is related to the fact that the alkaline metals included in the perovskite lattice are prone to form carbonates [57]. Balachandran *et al.* [58] shows how a hollow fiber dense membrane for the partial oxidation of methane (POM) reaction, failed during operation due to the formation of SrCO₃ and a mixture of cobalt and iron oxides thus collapsing the perovskite structure. Similar results were found by Yi *et al.* [59] when tested a Sr_{0.95}Co_{0.8}Fe_{0.2}O_{3-δ} membrane under air stream containing CO₂ and H₂O. Other studies did not reach the membrane failure but a remarkable decrease of the oxygen flow when CO₂ was introduced in the process [58, 60]. Homonnay *et al.* [61] by using Mossbauer spectroscopy studied the formation of carbonates in CO₂ rich atmosphere. They found that CO₂ interacts preferentially with Co due to the lower coordination of this element. In fact, Co is envisaged as the weakest link of the BSCF regarding the mechanical and chemical stability. Co ions are easy to reduce in a reductive atmosphere and the phase change is accompanied with destroying of the material phase structure and oxygen permeability. These reasons have motivated several researching groups to develop cobalt-free perovskite mixed conducting membranes with enhanced chemical stability such as Ba-Ce-Fe [62] or Ba-Sr-Zn-Fe [63]. Despite their greater stability, none of these solids could achieve the oxygen flux of the cobalt containing systems.

Arnold *et al* [57] reports one of the most complete studies of the influence of CO₂ on the BSFC membrane performance. A detailed analysis of the microstructure of the spent BSFC membrane was used to understand the CO₂ poisoning. These authors demonstrated that the use of CO₂ as pure sweep gas at 875 °C results in an immediate end of the oxygen permeation flux. However this behaviour was found to be reversible and complete oxygen flux recovered after switching the sweeping gas to helium. Upon

exposure of the BSCF membrane to CO₂ for 4300 minutes a careful inspection of the microstructure indicates its surface decomposition up to 40-50 μm depth Figure 3 shows several SEM images underlining the changes provoked by the CO₂ attack and the formation of a surface carbonate layer.

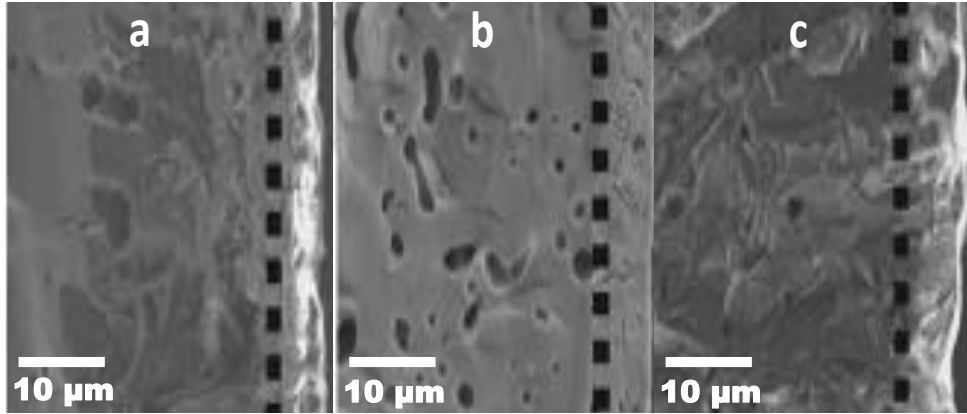


Figure 3. SEM analysis of the permeate side of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membrane. (a) 100 min with pure CO₂ as sweep gas; (b) after 100 min. recovering in He; (c) after 4300 min exposed to CO₂. (Images adapted from ref [57])

The picture sequence in Fig 4 reveals that the oxygen flux recovering after He treatment is associated to the perovskite reconstruction. Furthermore the XRD data together with the EDXS study presented in Arnold's paper clearly state the formation of a mixed barium strontium carbonate (Ba_xSr_{1-x})CO₃ layer *ca.* 5 μm thick responsible for the oxygen permeation drop.

The situation gains complexity when CO₂ and H₂O are fed simultaneously. On one hand, these molecules compete with oxygen for the adsorption sites in the membrane surface limiting the rate of the oxygen splitting and thus decreasing the oxygen flux. Yan *et al.* [64] found that the adsorption of CO₂ is promoted in the presence of H₂O in an extensive TPD study. The CO₂ desorption profile after adsorbing CO₂ in the presence of O₂ and H₂O exhibits a broad profile ranging from 250-500 °C that they

ascribed to bicarbonate species. Unfortunately undoubtedly identification of these bicarbonate species was not possible by any structural technique, although new crystalline phases, as for example BaCoO_2 , form suggesting that the perovskite structure upon CO_2 exposure is disrupted. Their data allow conclude that water enhances the CO_2 poisoning effect. The chemical stability of the BSCF on the presence of both CO_2 and H_2O depends on the amount of Ba. Since BaCO_3 is thermodynamically more stable than SrCO_3 [65,66] the isomorphic substitution with Ba has to be optimized to modulate the BSCF stability. Yan's study [64] revealed that the CO_2 adsorbed on $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ increases as the barium concentration increases (from 0.3 to 1) thereby affecting the membrane stability. On the other hand, the stabilization energy of barium perovskite is largely more negative than that of strontium perovskite. Therefore in balance, the stability against CO_2 poisoning is essentially the same for Sr and Ba perovskites [67].

The main strategy to face carbonate formation is to modify the perovskite structure by doping. The idea is simple and effective: modulation of the acid/base properties of the membrane to make it less sensitive towards CO_2 poisoning. Playing with ion deficiencies at the A-site may be an option. Lanthanum is often employed to replace barium (LSCF family), nevertheless this modification does not solve the problem since the remaining strontium would form carbonates [68]. An alternative is the use of stabilizing ions at the B-position. Martynczuk *et al.* [67], follows this strategy to prepare a Zn-doped BSF perovskite (BSFZ) obtaining valuable results in terms of stability and oxygen permeation flux. The use of a divalent metal like Zn promotes the oxygen permeability due to the higher ionic conductivity. They achieved good stability maintaining the oxygen permeation flux ($0.98 \text{ mL min}^{-1}\text{cm}^{-2}$) during 100 h at 950°C . However, after sweeping with pure CO_2 the oxygen permeation flux decreases

dramatically [57]. Upon CO₂ exposure a noticeable modification of the membrane microstructure occurs, mixed barium strontium carbonate forms together with a mixture of hexagonal, cubic and tetragonal perovskite with ZnO near grain boundaries. After regeneration tetragonal and cubic perovskite remained as major phases pointing that the hexagonal perovskite is unfavourable for oxygen permeation. These Zn-doped materials showed fully reversible CO₂ poisoning effect. CO₂ tolerant SCF membranes were developed by replacing at least 10% of Co and Fe by Ti or Ta at the B-site [69, 70]. XPS data of O 1s for Ta and Ti doped membranes reveals a shift towards higher binding energies in comparison to the parent membranes, suggesting lower charge density and consequently higher difficulty to donate electrons (lower basicity) of the M-O bond. Both Ta and Ti doped membranes exhibited a promising stability. In counterpart, slight decrease of the permeation flux was detected.

The BSCF membranes unavoidably suffer for CO₂ poisoning since alkali earth metal tend to form carbonates. Disruption of the perovskite structure is the immediate consequence of the formation of carbonates that damage the membrane performance. So far there is no membrane in the market able to stand CO₂ preserving the same oxygen flux. Nevertheless a reasonable membrane design (doping strategy) orientated towards basicity depletion improves the CO₂ resistance and CO₂ tolerant membranes can be obtained but with lower permeation flux. Nevertheless, for industry it could be worthwhile to get a stable membrane at the expense of sacrificing some oxygen permeation.

Similar strategies were adopted for the LSCF perovskite materials family. The concept of replacing higher contents of alkaline earth metals at the A site with rare earth cations results interesting to face the CO₂ poisoning effects. Rare earth cations are similar in size to alkaline-earth cations and more important their carbonates decompose at lower

temperatures [2]. Recently Tan *et al.* [71] developed a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane able to stand high concentration of CO_2 at 950 °C with enough oxygen permeation. Despite the good performance of this membrane, carbonate formation due to strontium carbonate segregation was observed resulting in an “inactive” superficial layer 1.4 μm depth. With the aim to avoid SrCO_3 formation, some other cations were introduced; for example, well performing $\text{La}_{1-x}\text{Ca}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes were proposed by Efimov *et al.* [72] exhibiting sufficient CO_2 resistance. Very recently, Partovi *et al.* [73] developed a new type of membrane using Pr as a dopant. In comparison with the extensively studied LSCF material, the PSCF membrane showed higher permeation flux since Pr^{3+} cation is smaller than La^{3+} thus decreasing the energy barrier for oxygen migration. Apart from the steric perspective, the polyvalent character of Pr ($\text{Pr}^{3+}/\text{Pr}^{4+}$) boosts molecular oxygen dissociation easing the superficial reaction. This membrane successfully withstands CO_2 attack maintaining high oxygen permeability and presenting a good candidate for oxyfuel applications.

As for the BSCF family, B-site substitution improves the stability towards CO_2 -rich atmospheres. Sirman [74] established that the CO_2 tolerance of perovskites oxides with different B-cations follows the order: $\text{Ga} > \text{Cr} > \text{Mn} > \text{Fe} > \text{Co}$. According to this, iron substitution by gallium, which results in a new family of materials (LSCG), appears to be a promising alternative to LSCF membranes [75-77].

Even though the doping strategy has been the most intensively studied, there are other different approaches for preventing the CO_2 poisoning of MIEC and merits some comments at this point. A fairly new trend to develop CO_2 -robust membranes is based on the dual-phase systems. These materials combine the best characteristics of different compounds in order to achieve a large oxygen permeability and relatively good chemical and mechanical stability at elevated temperatures. The composite materials

consist of an electron conducting material, which allows the percolation of electrons, and an ionic conductor that transports the oxygen ions through the membrane. For example García-Torregrosa *et al.* [78] designed a protective thin layer for LSCF ceramic membranes using spray pyrolysis. The shielding layer was composed by Ga doped ceria (CGO) and it remarkably increases the CO₂ tolerance of the bare LSCF. The permeation flux of the composite system was smaller than that of the primary LSCF membrane; however the great chemical stability compensates the permeability drop. Similar results using the other reference family of MIECs (BSFC) as a main component and a protective layer based on Sr, Fe and Nb oxides (SFN) was also recently reported [79]. Figure 4 compares the performance of the BSFC “nude” membrane vs. the SFN-coated membrane.

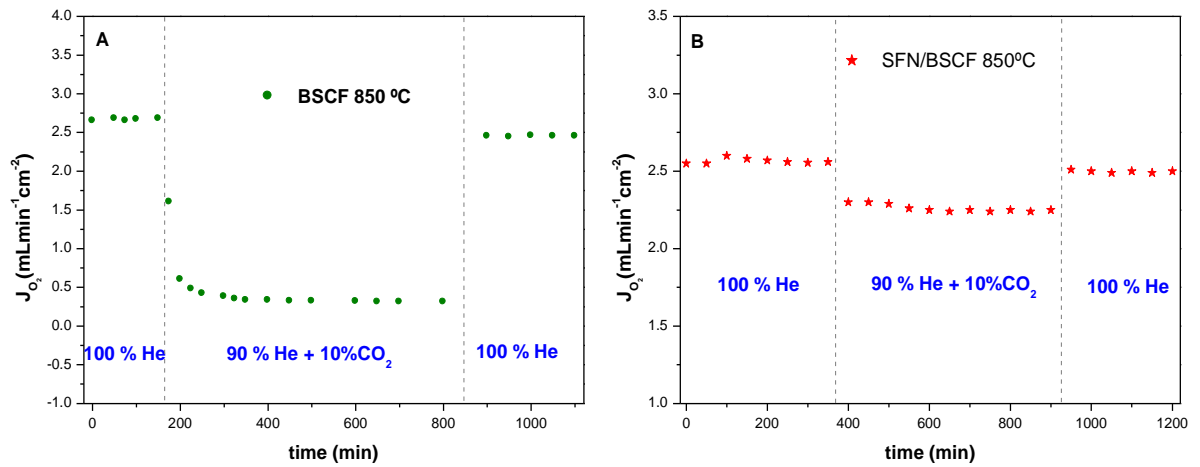


Figure 4. Comparative behavior of BSFC and SFC-BSCF membranes towards CO₂ exposition (adapted from ref [79])

In the same context, Balaguer *et al.* [80] proposed a mixed oxide membrane based on NiFe₂O₄-Ce_{0.8}Tb_{0.2}O_{2-δ} with extraordinary stability under SO₂ and CO₂ atmospheres. Afterwards the same research group employed the mixed oxide as a protective layer on

a conventional LSCF membrane [81]. The coating (8 μm -thick layer of $\text{NiFe}_2\text{O}_4\text{-Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$) permits elevated and stable oxygen flux under 50% of CO_2 during 150h.

No matter the selected concept, important advances are made in the recent years, and a variety of promising materials are reported. Nevertheless the presence of more gases has to be taken into consideration.

3.2 Tolerance towards SO_2

The influence of carbon dioxide on the oxygen permeation of MIECs has been extensively studied in comparison to the effect of other gases, such as SO_2 , which can also be present in the gas streams. Of course CO_2 will be the major component of a hypothetical gas mixture where MIEC should work (for instance oxyfuel process). Nevertheless SO_2 influence must be mandatorily evaluated and represents one of the biggest concerns in this area. For example the SO_2 concentration in the flux gas can be situated at around 400 ppm or even higher than 1000 ppm, as reported before the scrubber system in some power plants in China [82]. Up to 2011 few reports can be found dealing with membrane operation in SO_2 environments. However in related topics, as for example in catalysis several studies revealed the formation of sulphates and sulphides for lanthanum perovskites catalysts [82, 3]. Engels *et al.* [84] report the first study on the SO_2 influence on MIEC permeability. They demonstrated the detrimental effect of SO_2 on the oxygen permeability of BSFC, SCMF and La_2NiO_4 materials. Such a negative outcome was attributed to the formation of sulphate salt porous layer that difficult the oxygen transport. Gao *et al.* [85] studied in details the SO_2 influence on the popular LSCF membranes family. At temperatures above 850 $^\circ\text{C}$ when the oxygen flux becomes relevant, the membrane exposed to SO_2 is seriously deactivated (Figure 5). SEM pictures revealed a significant degree of corrosion in the

membrane surface upon SO₂ exposition. More dramatically, the caused damage was irreversible. After removing the SO₂ from the sweeping gas and cleaning the surface with acid, the oxygen flux was not recovered.

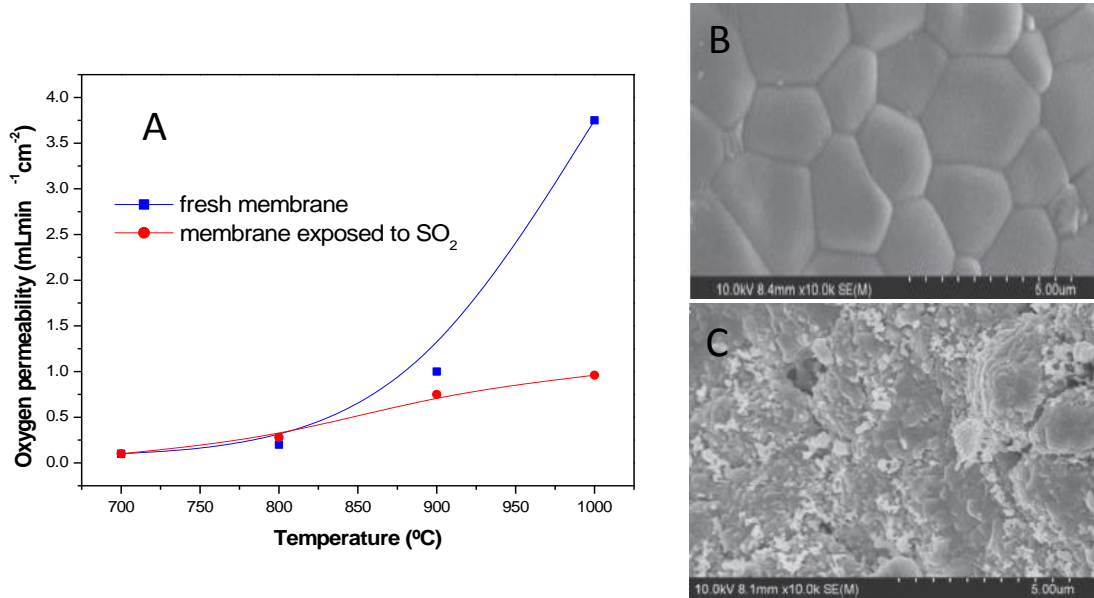


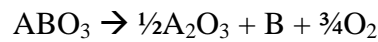
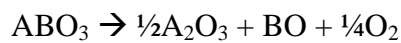
Figure 5. Effect of SO₂ on the LSCF membrane. (a) oxygen permeation flux; (b) SEM image of the fresh membrane; (c) SEM image of the membrane after SO₂ exposure. (adapted from ref. 85)

This huge oxygen permeability drops was associated to two main reasons; i) the formation of a corrosive layer and ii) to the extraction of Sr from the perovskite to form SrSO₄. The disruption of the perovskite structure affects the ion transport mechanism. In addition, SrSO₄ and other metal oxides formed in this process are not ionic conductive species [85]. On the other hand, Waindich *et al.* [86] employed very realistic conditions (61% CO₂, 9% O₂, 29.8 %H₂O and 0.2% SO₂) to test BSCF and LBCF systems. They observed severe corrosion for both types membranes, disruption of the perovskite structure and oxide segregation, e.g. Co₃O₄. In agreement with previous results, they reported strontium and barium carbonates formation accompanied by the corresponding alkaline sulphates. The corrosion was even enhanced under humid

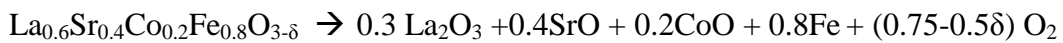
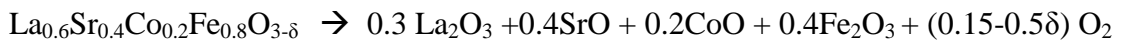
conditions. The dual phase membrane presented in ref [80] is one of few membranes developed up to date that exhibits some tolerance towards SO₂. Nevertheless its features are not enough for a real application. In spite of the limited literature regarding SO₂ influence on the MIEC performance, the results obtained so far indicates that SO₂ is more aggressive than CO₂. Low amounts of this compound may provoke irreversible damages on the membrane, which reduce seriously the oxygen permeability. Further investigation is still needed to overcome this problem.

3.3 Tolerance towards reductive environments

Together with CO₂ and SO₂ (with or without water) the success of membrane technology requires also stability under reductive conditions. In particular, when the LSCF and BSFC are employed as catalytic reactors for POM the CH₄ rich atmosphere may corrode the permeate side of the membrane [87]. For example Bouwmeester [14] reported that a Cr doped LSCF membrane failed under long-term operation (350 h) in POM reaction at 900°C. Under reductive atmospheres two general decomposition reactions may happen on an ABO₃ perovskite [88]:



In the case of the LSCF membranes the reduction can be described as follows:



Similar equations can be considered for the BSCF family. In any case partial reduction of the perovskite structure will affect the oxygen permeability. Indeed, as reported by Shao *et al.* [89] that Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} is unstable under 5% H₂-Ar stream. The perovskite was reduced to Fe, Co, BaO, SrO, Ba(OH)₂ and Sr(OH)₂ indicating the lack

of robustness of these membranes under reductive environments. On the hand, when CH₄ is the reductive agent, the membranes exhibit better resistance and even in some case the oxygen permeation flux is increased. For example, Lui *et al.* [90] prepared a hollow fiber LSCF system for which the oxygen permeability was broadly improved when CH₄ is employed as sweep gas [44]. Such a positive effect was associated to the surface etching resulting in membrane surface deterioration, hence resulting in enhanced surface area to facilitate oxygen permeation. A general strategy to extend the operation life of a membrane under reductive conditions is the use of less reducible cations as dopants. Zr⁴⁺, Ga³⁺ or Nb⁵⁺ represents valuable alternatives [39]. A recent work of Kathiser *et al.* emphasizes the successful behaviour obtained with a Ga-doped LSC membrane under CO₂ and CH₄ streams [29]. Significant and stable oxygen permeability was attained under harsh environment with boosted O₂ flux in the presence of CH₄. These results indicate that tolerance towards reductive atmospheres (concretely CH₄-rich streams) can be reached with the proper chemical design of the ceramic membrane.

4. Where the future is?

The application of perovskite membranes in the oxyfuel or other oxygen requiring processes is a question of time. The BSCF and LSCF families of perovskite membranes seem to be preferred on the oxygen flux point of view. Nevertheless for a real application *e.g.* the use of these membranes in an oxyfuel plant the stability prevails over the permeation flux diminution. The increase of the stability could imply a total change of the landscape; the replacement of BSCF for LSCF or cobalt-free membranes may be a possible route. The use of more membranes in a microchannel stacking configuration or more complicated engineering designs could compensate the decrease of the oxygen flux in these cases. The dual phase systems approach is another possible route. This approach tries to take advantage of the best properties of at least two

different components to achieve large oxygen permeability and sufficient chemical/mechanical stability. However the dual phase concept brings a new challenge to the membrane field: the compatibility. For example, thermal expansion coefficients of both materials should be considered for mechanical compatibility. Chemical compatibility is also a factor to consider. Using these premises as starting point the new generation of dual-phase MIECs may fulfill the chemical stability requirements for a real application.

The SO₂ must be considered in the membranes testing devices more frequently (as CO₂ is well implemented right now). The development of SO₂ tolerant dense ceramic membranes is still a chemical challenge to face.

The solution might be hidden just behind the door.

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